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Electrostatic assembly of superwetting porous nanofibrous membrane toward oil-in-water microemulsion separation

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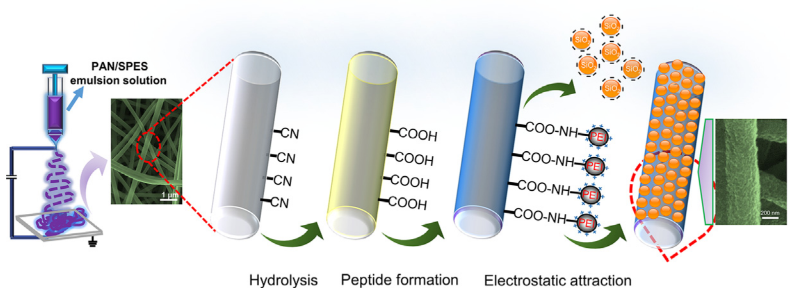
HIGHLIGHTS

- A superwetting nanofibrous membrane with strong corrosive resistance was prepared via co-electrospinning.
- A highly charged polyethyleneimine was successfully grafted onto the hydrolyzed PAN/SPES nanofibrous membrane surface.
- An electrostatic assembly method was used to construct the hierarchically structured nanofibrous membrane.
- The composite nanofibrous membrane shows robust superwetting performance with a WCA of 0° and an UOCA of 161°.

GRAPHICAL ABSTRACT



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ABSTRACT

Creating a lotus-leaf-structured membrane surface with nano/microstructures plays a key role in the development of functional membranes for oil/water separation; however, fabrication of such membranes with uniform and compact nano/microstructures *via* an efficient and facile method have demonstrated to be challenging. Herein, a superwetting nanofibrous membrane with strong corrosive resistance was prepared via co-electrospinning of polyacrylonitrile/sulfonated polyethersulfone nanofibrous membrane (PAN/SPES NFM), amination of PAN and subsequent electrostatic assembly of lotus-leaf-structure by binding the negatively charged silica nanoparticles (SiO_2 NPs). Benefiting from the changes in pore size distribution and surface structure of nanofibrous membrane, the optimal membrane is endowed with an intriguing superhydrophilicity of 0°, an underwater superoleophobicity of 161°, and an outstanding oil proof pressure of 95.5 kPa. These fantastic features inspired the membrane to effectively separate the surfactant-stabilized oil-in-water microemulsion with a high water flux of 1852 ± 158 $L\,m^{-2}\,h^{-1}$ and a high separation efficiency of 99.6% when a vacuum driven pressure of 10 kPa was applied. The layer-by-layer assembly method utilized in the construction of membrane roughness is expected to be applicable to a wide range of other selective wetting separation fields.

1. Introduction

With the acceleration of industrialization and speed of internationalization, the industrial oily wastewater and catastrophic oil pollution such as the Deepwater Horizon oil spill in the Gulf of Mexico pose a serious threat to the marine environment and aquatic ecosystem

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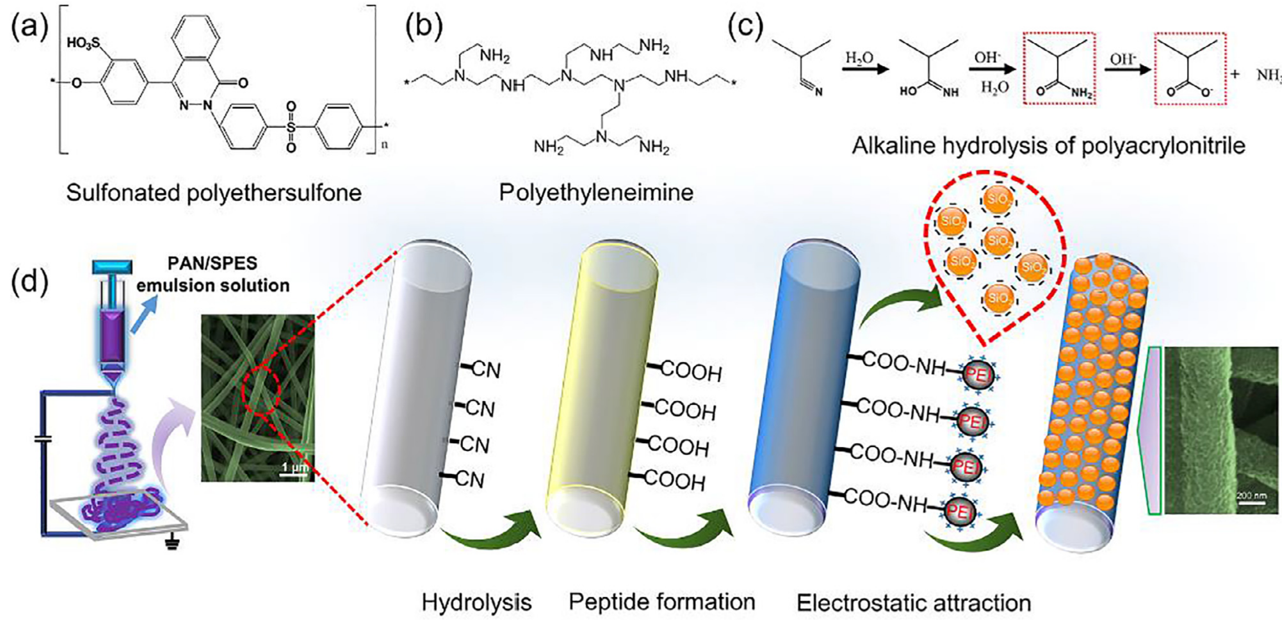

Fig. 1. Chemical structures of (a) SPES and (b) PEI. (c) The hydrolysis reaction of PAN. (d) Schematic showing the fabrication procedures of hierarchically structured nanofibrous membrane.

[1–3]. Therefore, efficient and cost-effective functional membrane to separate oil/water mixture is highly desired. Recent progress in developing interfacial membrane with selective wettability including hydrophobic/oleophilic (oil removing) or hydrophilic/oleophobic (water removing) interfaces has been flourishingly developed due to the easy preparation, mild operation and comparative low cost [4–7]. However, to the best of our knowledge, the oil removing type membranes can be easily fouled or even blocked by oils, resulting in the continuous decrease of separation flux and serious limitation of recycle usage [8–10]. Hence, designing a superhydrophilic/underwater superoleophobic (water removing) membrane can be suggested as an alternative and promising method to address the above-mentioned issues in oil/water separation [11,12].

Water flux and membrane fouling are the two critical factors that directly affect membrane durability for the practical application in oil/water separation [13,14]. Generally, water flux is highly determined by the pore structure and membrane surface hydrophilicity [15–18]. Phase inversion membrane in combination with a hydrophilic surface was first employed to fabricate superwetting oil/water separation membrane [19–22]. Unfortunately, the closed pore structured membranes mentioned above need strong external force (~1 bar) to driven the permeation of water across the membrane. Terribly, under the strong external driven force, the oil droplets can wick into the membrane pores after long-time operation, resulting in the continuous decrease of separation efficiency. In the past ten year, electrospinning technique has been demonstrated to be a facile and versatile method to manufacture three-dimensional structured macroporous membranes *via* layer-by-layer (LBL) accumulation of fibers, which can effectively solve the problem that traditional closed structured membrane faced [23–27]. Moreover, the fiber compositions, morphologies, as well as pore structure can be easily regulated by the design of electrospinning solution and machining parameter. The fouling of oil/water separation membrane is another crucial issue [28,29]. According to the Young's equation, it has been demonstrated that a micro/nanoroughness membrane surface in combination with a hydrophilic layer can effectively improve the membrane permeability [30,31]. In addition, the Cassie mode also demonstrated that the increasing membrane surface roughness can significantly improve the underwater oil contact angle (UOCA), thus reducing the membrane pore fouling [32,33].

Intending to obtain superwetting nanofibrous membranes with hierarchical roughness and interlinking open cell structure, the co-electrospinning of complex polymer/nanoparticles solution seems to be the most popular for fiber roughness construction. Unfortunately, most nanoparticles sacrificed in the cylindrical fibers not only reduce the utilization of nanoparticles, but also deteriorate the mechanical strength of membrane substrate [34–36]. In addition, the agglomerated nanoparticles are easy to leak and result in the secondary contamination of water bodies. Recently, the electrostatic attraction method utilizing different charges between the membrane substrate and the nanoparticles has been considered as one of the most effective ways for membrane roughness construction [37–39]. For example, the polymer porous membrane was first etched by NaOH to form reactive functional groups, followed by grafting highly positive charged amine functional groups. Differing from the stabilized phase conversion membrane, the nanofibrous membrane assembled via LBL accumulation of cylindrical nanofibers are easily agglomerated by each other when treated at high-temperature alkaline aqueous solution, finally blocking the membrane pores. Sulfonated polyethersulfone (SPES) is a special functional polymer that interlinked the ether and the sulfone to the benzene, thereby leading to excellent thermal property and strong antioxidation ability [40]. Therefore, it is promising to construct SPES based nanofibrous membrane (NFM) with interconnected porous structure and strong antioxidation performances for preparing highly positive charged amine functionalized membrane. However, the processibility of SPES with amine functional groups is generally inferior to that of commodity polymers, rendering the challenge in fabrication of hierarchically structured superwetting oil/water separation membrane.

In this contribution, a superhydrophilic and underwater superoleophobic nanofibrous membrane was prepared via co-electrospinning of polyacrylonitrile/sulfonated polyethersulfone (PAN/SPES) emulsion solution, amination of PAN, and LBL assembly of silica nanoparticles (SiO_2 NPs) *via* electrostatic attraction. The detailed chemical structures and fabrication procedures are shown in Fig. 1. It is worth to note that the SPES used here was aimed at serving as the fiber skeleton to maintain membrane stability, and the PAN after hydrolysis was aimed at providing functional groups to graft highly positive charged polyethyleneimine (PEI). The modified nanofibrous membrane can uniformly and compactly bind the negatively charged SiO_2 NPs onto the fiber surface without flaws. Significantly, the mechanical property, antifouling performance, as well as the separation performance of